

The partial translation of JP 2003-243028

1

(11) Publication Number: 2003-243028

(43) Date of Publication of Application: August 29, 2003

(51) Int. Cl.⁷

H 01 M 10/40

5 H 01 G 9/058

H 01 M 4/02

4/60

(21) Application Number: 2002-36172

(22) Application Date: February 14, 2002

10 (72) Inventor: FUCHIGAMI Toshio

(72) Inventor: ATOBE Masato

(72) Inventor: ISHII Hideki

(72) Inventor: SEKIGUCHI Kei

(72) Inventor: TAKADA Naokado

15 (71) Applicant: Central Glass Co., Ltd.

(54) TITLE OF THE INVENTION: ELECTROCHEMICAL DEVICE

[CLAIMS]

20 1. An electrochemical device at least including a positive electrode, a negative electrode, and an ion conductor filled between the electrodes, the positive or negative electrode or both comprising a conductive polymer, and the ion conductor comprising an ionic liquid.

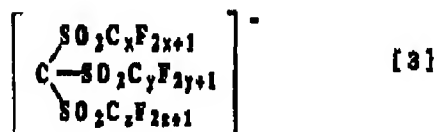
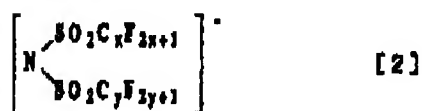
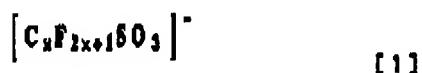
25 2. The electrochemical device according to claim 1, wherein the conductive polymer is synthesized by electrolytic polymerization of a polymerizable compound in an ionic liquid.

30 3. The electrochemical device according to claim 1 or 2, wherein the ionic liquid included in the device or an ionic liquid used in synthesis of the conductive polymer by electrolytic polymerization is selected from the group consisting of a nitrogen-containing onium salt, a

sulfur-containing onium salt, and a phosphorus-containing onium salt.

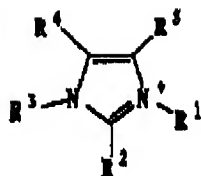
4. The electrochemical device according to any one of claims 1 to 3, wherein the conductive polymer is selected from the group consisting of polypyrrole and a derivative thereof, and polythiophene and a derivative thereof.

5. The electrochemical device according to any one of claims 1 to 4, wherein the ionic liquid has at least one anion selected from the group consisting of anions represented by general chemical formulae [1], [2] and [3]:



wherein each of x, y and z independently represents an integer of 1 to 8.

6. The electrochemical device according to any one of claims 1 to 5, wherein the ionic liquid has at least one cation selected from the group consisting of a quaternary alkylammonium ion and an imidazolium ion represented by general formula [4]:



[4]

wherein each of R¹, R², R³, R⁴ and R⁵ independently represents a C1-C20 alkyl group or a hydrogen atom.

- 5 7. A method of synthesizing a conductive polymer for the electrochemical device according to any one of claims 1 to 6, comprising electrolytic polymerization of a polymerizable compound in an ionic liquid so as to deposit the conductive polymer on an electrode.

10

[DETAILED DESCRIPTION OF THE INVENTION]

- Line 14 of Column 2 to Line 12 of Column 3

[0001]

- 15 The present invention relates to an electrochemical device such as a lithium cell, lithium ion cell, electric double-layer capacitor, or electrochromic display.

[0002]

- 20 Nowadays, with the evolution of portable equipment, there has been active development of electrochemical devices, which utilize electrochemical phenomena, as their power supplies, such as cells, capacitors, and wet solar cells. Examples of electrochemical devices other than power supplies include electrochromic displays (ECD) in which a color change occurs
25 through an electrochemical reaction.

[0003]

- 30 In general, such an electrochemical device is composed of a pair of electrodes and an ion conductor filled between them. Examples of materials of the electrodes include a wide variety of materials that can undergo reversible oxidation-reduction

reactions, such as metals, oxides, nitrides, sulfides of transition metals, and carbon materials. Combinations of these materials are used for positive and negative electrodes, and in general, metals and carbon materials are used for negative electrodes while transition metal compounds are used for positive electrodes in many cases. However, transition metals have a problem in terms of their reserves and may also pollute the environment when discarded.

[0004]

10 Meanwhile, the ion conductor of the electrochemical device
is a solution of a salt (electrolytic solute) in a solvent.
When dissolved in the solvent, the electrolytic solute is
15 dissociated into cations and anions, resulting in ionic
conductivity. In order to obtain the required level of ion
conductivity for the device, it is necessary to dissolve a
sufficient amount of the electrolytic solute in the solvent.
In many cases, water or an organic solvent is used as the solvent.
Examples of the organic solvent include ethylene carbonate,
propylene carbonate, dimethyl carbonate, diethyl carbonate,
20 ethyl methyl carbonate, γ -butyrolactone, dimethoxyethane,
diethoxyethane, and tetrahydrofuran. Unfortunately, water
is susceptible to oxidation-reduction reactions, and
therefore only limited electrode materials can be used in this
case. In addition, organic solvents as mentioned above are
25 generally highly volatile and flammable and thus are
categorized as flammable substances. Accordingly, when used
in a relatively large device such as a power storage device
or a power supply for an electric vehicle, they have a problem
of low safety in an emergency such as, in particular, overcharge,
30 over-discharge or short, or even under high-temperature
conditions.

[0005]

In consideration of the above problems of the prior art, the present inventors have conducted intensive studies to

provide an electrochemical device that is environment-friendly and highly safe. As a result, the inventors have found that a useful electrochemical device can be obtained by using a conductive polymer as a positive or negative electrode material, and an ionic liquid as an ion conductor between the electrodes.

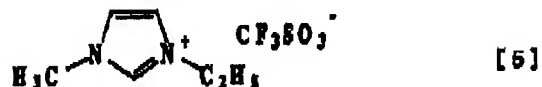
- Lines 32-38 of Column 5
[0014]

10 In the case of using a conductive polymer obtained by such a method for an electrochemical device, the device has basic components including an ion conductor, a negative electrode, a positive electrode, a current collector, a separator, and a container. Specific examples of the electrochemical device
15 according to the present invention include lithium cells, lithium ion cells, capacitors, electrochromic displays, wet solar cells, and sensors.

- Line 23 of Column 9 to Line 48 of Column 10
20 (Example 1)

Pyrrole was dissolved in 1,3-ethylmethylimidazolium triflate represented by formula [5] to a concentration of 0.1 mol/dm³.

[0031]



25

[0032]

The obtained solution was charged in a beaker cell equipped with a pair of platinum electrodes (1×1 cm²) as working and counter electrodes and an SCE (saturated calomel electrode)
30 connected through a salt bridge as a reference electrode. Electrolytic polymerization was carried out by potential scan

at a scan rate of 100 mV/s in a potential range of -0.8 to +1.2 V (vs. SCE) for 20 cycles. Polypyrrole deposited on the working electrode was washed well with acetonitrile, and then dried under reduced pressure, whereby a polypyrrole film on the platinum electrode was obtained.

[0033]

Next, in order to investigate the electrochemical activity of the electrode, the obtained polypyrrole (coating on the platinum electrode) as a working electrode, a platinum counter electrode, and a reference SCE (saturated calomel electrode) connected through a salt bridge were immersed in 1,3-ethylmethylimidazolium triflate, and subjected to potential scan at a scan rate of 100 mV/s in a potential range of -0.6 to +1.0 V (vs. SCE). As a result, reversible oxidation-reduction reactions occurred with an oxidation peak at about +0.2 V and a reduction peak at about -0.2 V. The oxidation peak current was 6.0 mA in the first cycle, and was 5.0 mA in the 50th cycle, and stable oxidation-reduction reactions could be repeated without degradation.

(Example 2)

Pyrrole was dissolved in 1,3-ethylmethylimidazolium triflate to a concentration of 0.2 mol/dm³. The obtained solution was charged in a beaker cell equipped with a pair of aluminum electrodes (3×3 cm²) as working and counter electrodes and an SCE (saturated calomel electrode) connected through a salt bridge as a reference electrode. Electrolytic polymerization was then carried out at a constant potential of +1.2 V (vs. SCE). Polypyrrole deposited on the working electrode was washed well with acetonitrile, and then dried under reduced pressure, whereby a polypyrrole film on the aluminum electrode was obtained.

[0034]

Next, a cell was prepared with the obtained polypyrrole electrode as a positive electrode, a natural graphite negative

electrode, a solvent of trimethyl propylammonium bis(trifluoromethanesulfonyl)imide represented by formula [6]:

[0035]



5

[0036]

and a supporting electrolyte of lithium bis(trifluoromethanesulfonyl)imide. Charge-discharge tests were actually performed on the cell. The test cell was prepared as follows.

10

[0037]

Regarding the polypyrrole positive electrode, the polypyrrole deposited on the aluminum electrode plate after polymerization was used without modification as a positive electrode. Meanwhile, natural graphite powder and poly(vinylidene fluoride) (PVDF) as a binder were mixed at a weight ratio of 90:10, and N,N-dimethylformamide was added to the mixture to give a slurry. This slurry was applied to a copper foil, and dried at 150°C for 12 hours. The obtained product was used as a negative electrode. Regarding the separator, a polyethylene separator was used. The separator was impregnated in advance with a trimethyl propylammonium bis(trifluoromethanesulfonyl)imide solution containing 1.0 mol/dm³ of lithium bis(trifluoromethanesulfonyl)imide, and then assembled with other components into a cell.

15

20

25

[0038]

Next, galvanostatic charge-discharge tests were performed under the following conditions. Both charge and discharge were performed at a current density of 0.35 mA/cm² and an ambient temperature of 25°C, charge was performed up to +4.2 V, and discharge was performed up to +3.0 V (vs. Li/Li). As a result, the initial capacity was 69 mAh/g dry polymer weight. The

30

charge/discharge cycle was repeated 500 times, and the capacity in the 500th cycle was found to be 87% of the initial capacity.

[0039]

- 5 In addition, the used electrolytic solution was applied to a filter paper, and a flame test was performed by applying a flame. The result showed that the paper did not burn at all.

- Lines 33-38 of Column 12

10 [0046]

[Effects of Invention]

- 15 The electrolyte of the present invention relates to electrodes and an ion conductor for an electrochemical device such as a lithium cell, lithium ion cell, or electric double-layer capacitor. The present invention provides an electrochemical device with high safety and excellent performance.